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# XIV.

## CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

### A REVISION OF THE ATOMIC WEIGHT OF STRONTIUM.

#### FIRST PAPER: THE ANALYSIS OF STRONTIC BROMIDE.

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Presented June 9, 1894.

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#### EARLIER WORK.

A GLANCE at published results shows that the atomic weight of strontium has not been investigated for thirty-five years. The early determinations, good enough for their time, show variations which render them quite unsatisfactory to-day; and the case is parallel in every respect to that of barium, which has formed the subject of two recent papers.\*

The oldest experiments of any note upon the atomic weight of strontium are those of Stromeyer,† who measured, in 1816, the gas evolved from strontic carbonate upon its decomposition by an acid. The result, which is only of interest historically, gives  $Sr = 87.3$ , if a litre of carbon dioxide weighs 1.977 grams under normal conditions.

At about the same time Rose‡ found that 181.25 parts of argentic chloride could be obtained from a hundred parts of strontic chloride,—data which indicated  $Sr = 87.31$ . Twenty-seven years afterward, in

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\* These Proceedings, XXVIII. 1; XXIX. 55.

† Schweig. J., XIX. 228; Meyer u. K. Seubert's Atomgewichte, p. 123.

‡ Poggendorff's Annalen, VIII. 189.

1843, Salvétat \* determined by loss of weight the carbon dioxide in strontic carbonate, and concluded that the metal must be 88.0, — a result which scarcely improved the situation.

Subsequently, in 1845, Pelouze † found the amount of silver necessary to precipitate a weighed amount of ignited strontic chloride; his results give the value  $Sr = 87.70$ . Thirteen years later Marignac ‡ repeated these experiments, determining also the amount of crystal water in crystallized strontic chloride, as well as the amount of strontic sulphate obtainable from the salt. Thus he found that 15.000 grams of crystallized strontic chloride yielded 8.9164 § grams of the anhydrous salt and 10.3282 grams of strontic sulphate; moreover, 15.000 grams of hydrated strontic chloride required 12.1515 grams of silver for precipitation. Another similar series of experiments upon the water of crystallization made its amount appear three milligrams more than before. These data give basis for a number of possible values for the atomic weight of strontium, ranging from 87.17 to 87.55, the individual figures being tabulated below.

In 1859 Dumas || published another determination of the ratio of strontic chloride to silver, the salt having been fused in a stream of hydrochloric acid. Altogether, 27.3435 grams of strontic chloride required in his hands 37.252 grams of silver, the individual values for strontium varying from 87.3 to 87.8. Since this time the subject has remained untouched.

Below is tabulated a list of the various determinations, grouped according to the ratios determined.

*The Atomic Weight of Strontium*

Oxygen = 16.000.

From the carbonate:

Stromeyer, 1816 . . . . .	87.30
Salvetat, 1843 . . . . .	88.00

Ratio of strontic and argentic chlorides:

Rose, 1816? . . . . .	87.31
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\* Comptes Rendus, XVII. 318.

† Ibid., XX. 1047.

‡ Liebig's Annalen, CVI. 168.

§ Corrected by L. Meyer u. K. Seubert, Atomgewichte, pp. 78, 79.

|| Liebig's Annalen, CXIII. 34.

Ratio of anhydrous strontic chloride to silver :

Pelouze, 1845 . . . . .	87.70
Marignac, 1858 . . . . .	87.48
Dumas, 1859 . . . . .	87.53

Ratio of crystallized strontic chloride to silver :

Marignac, 1858 . . . . .	87.52
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From the crystal water in strontic chloride :

Marignac, 1858 . . . . .	87.35
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Ratio of anhydrous and crystallized strontic chloride to strontic sulphate :

Marignac, 1858 . . . . .	87.2 to 87.6
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Selected by Clarke . . . . .	87.58
Selected by Meyer and Seubert . . . . .	87.5
Selected by Ostwald * . . . . .	87.5

A critical review of the list reveals a great lack of trustworthiness in all the figures. The values deduced from the carbonate, and those involving water of crystallization, may all be thrown out at once; and the results yielded by the displacement of hydrochloric by sulphuric acid are but little better. The series upon which most chemists have relied — the one based on the titration of the chloride by means of silver — is hopelessly vitiated by the imperfect execution of the method of analysis.† If any further proof of this uncertainty were needed, the following table, giving a comparison of the work of different experimenters upon other chlorides, would furnish it.

MOLECULAR WEIGHTS OF CHLORIDES BY THE METHOD OF GAY-LUSSAC.

	Pelouze.	Marignac.	Dumas.	Stas.	
				1st.	2d.
NaCl	58.434		58.468	58.506	58.503
KCl		74.539		74.583	74.600
NH <sub>4</sub> Cl	53.464	53.450		53.530	53.532

\* Much assistance in preparing this list has been obtained from the well known works of these authors. The figures have all been based upon the most recently accepted atomic weights.

† These Proceedings, XXIX. 80 *et seq.*

Thus, Pelouze, Marignac, and Dumas all obtained low results with the method of Gay-Lussac; in fact, the error sometimes exceeded the tenth of one per cent. The cause of this error, which appeared also in the work of these experimenters upon barium, has already been pointed out in another paper.\*

We are thus led to infer that the true molecular weight of strontic chloride must exceed the usually accepted value 158.4 by about one tenth of one per cent, and that the true atomic weight of strontium must be nearly 87.7. This inference is confirmed by the result of the investigation now to be described.

The balance and weights, and the methods of weighing and of tabulating results employed in the work recounted below have already been described in sufficient detail.† The balance seems to have increased slightly in sensitiveness during its four years' work, owing perhaps to the smoothing of microscopic roughnesses in the bearings. It is almost needless to say again that the weights were carefully standardized from time to time, and the small, surprisingly constant corrections were always applied. The correction to the vacuum standard was calculated by the usual formula:

$$\left( \frac{0.001293}{\text{sp. gr. substance}} - 0.000156 \right) \frac{H}{760} \frac{273^\circ}{273^\circ + t^\circ} = \text{correction in grams for 1 gram of substance.} \ddagger$$

The values thus calculated for the appropriate substances at 20° and 760 mm. were as follows:

*Correction to be applied to One Gram of Substance.*

	Gram.
Silver . . . . .	—0.000031
Argentio bromide . . . . .	+0.000043
Strontic bromide . . . . .	+0.000141

The general plan of the following work was similar to that adopted in the case of barium. For obvious reasons the bromide of strontium was chosen as the starting point; and the investigation began with a study of the properties of the salt, in order to determine its fitness for the purpose.

The atomic weight of silver is assumed to be 107.93, and that of bromine 79.955, unless a definite statement to the contrary is made.

\* These Proceedings, XXIX. 80.

† These Proceedings, XXVI. 242; also XXVIII. 5.

‡ H = atmospheric pressure;  $t^\circ$  = atmospheric temperature at the time of weighing; 0.000156 = standard weight of air displaced by 1 gram of brass.

## PROPERTIES OF STRONTIC BROMIDE.

The properties of the bromide of strontium resemble very closely those of the corresponding salt of barium. As is well known, however, the strontium salt usually crystallizes with six instead of with two molecules of water. The crystals, unlike those of the barium salt, are noticeably hygroscopic in ordinary air, so that they cannot be weighed with great accuracy; they melt easily in their own water of crystallization at about  $100^{\circ}$ . This latter fact renders more difficult the quantitative drying of the salts; indeed, in the few cases where the water of crystallization was determined, it was necessary to allow the crystals slowly to lose their water in a desiccator before ignition. Thus, it was found in the following experiment that five molecules of water were given off, the sixth having very little, if any, tension at ordinary temperatures.

	Grams.
Initial weight of strontic bromide . . . .	1.3305
Constant weight after three weeks over $\text{H}_2\text{SO}_4$ . . . .	.9926
Heated to $200^{\circ}$ for three hours . . . .	.9246
Loss of weight in dry air { Found . . . . = 25.41	
{ Calc. for 5 $\text{H}_2\text{O}$ = 25.33	
Additional loss on ignition { Found . . . . = 5.11	
{ Calc. . . . . = 5.06	

A week's standing in the air of the laboratory sufficed to supply again all the water which had been lost. These results point without doubt to the existence of a definite substance having the formula  $\text{SrBr}_2 \cdot \text{H}_2\text{O}$ , which is hygroscopic in the air and corresponds to the compound  $\text{BaBr}_2 \cdot \text{H}_2\text{O}$ , obtained in a similar way.\* The existence of this substance has already been inferred by Lescœur † from observations of the vapor tension of the crystal water. Anhydrous strontic bromide is perhaps even more hygroscopic than the corresponding salt of barium.

Strontic bromide melts to a transparent liquid at  $630^{\circ}$  (Carnelly), losing bromine in noticeable quantities if exposed to the air for some time at this temperature. Fused in a current of dry hydrobromic acid the salt soon recovers this lost bromine, and upon subsequent solution in water shows itself to be wholly neutral both to phenol phthalein and methyl orange. It will be seen that this fact is of the

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\* These Proceedings, XXVIII. 12, foot-note.

† Ann. de Chim. et de Phys., [6.], XIX. 553 (1890).

utmost significance. The cold fused transparent or translucent mass is much less hygroscopic than the powder from which it was made.

The importance of driving out every trace of water from the salt before weighing cannot be overestimated. Systematic experiments\* with baric bromide and chloride led to the conclusion that probably neither of these salts retains water at a red heat, and it was to be expected that the same fact might be true of the substance in hand. In order to test the point, four grams of very pure strontic bromide dried at about  $400^{\circ}$  were fused in a stream of hydrogen bromide. The mass *gained* nearly six milligrams in weight, showing that the loss of bromine in the air at  $400^{\circ}$  much more than counterbalanced a possible trace of water. Again, 11.2610 grams of the same specimen, dried at  $305^{\circ}$  until constant in weight, were found to weigh 11.2630 grams after fusion as before. Since these gains corresponded closely with losses of bromine found alkalimetrically in similarly heated but unfused samples, it is evident that very little if any water can be held by the dried salt. It has already been pointed out that no absolute proof of such a fact is possible;† and these experiments, together with the analogy furnished by the more manageable barium salts, seem to be the last resort. The apparatus used for these experiments will be described under the heading "Method of Analysis."

The specific gravity of anhydrous strontic bromide has been found by Bödeker to be 3.96. Since no more recent data regarding this constant could be found, another determination, described below, seemed to be needed. 3.2560 grams of a pure specimen which had been fused in the air and dried at  $200^{\circ}$  in the pycnometer were found to displace 0.6678 gram of toluol at  $24^{\circ}$ . Since the specific gravity of the toluol under these conditions, referred to water at  $4^{\circ}$ , was found to be 0.8618, that of the strontic bromide referred to the same standard must be 4.203. Again, 2.3065 grams of strontic bromide which had been fused in a stream of hydrobromic acid displaced 0.4699 gram of toluol, thus having a specific gravity of 4.229. The mean of these determinations, 4.216, was adopted as the basis of the reduction of the weighings to the vacuum standard.

Strontic bromide, like baric bromide and chloride, may be evaporated to apparent dryness over a free flame in a platinum dish without losing a trace of halogen. Experiment showed that, upon mixing pure bromide of strontium with small quantities of bromide of calcium and

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\* These Proceedings, XXVIII. 12; XXIX. 58.

† These Proceedings, XXVIII. 14.

barium and crystallizing the mixture, both impurities tended toward the mother liquors. Hence simple crystallization affords a method of eliminating the two most likely impurities.

The other properties of strontic bromide do not pertain especially to the present work.

#### PREPARATION OF MATERIALS.

*Strontic Bromide.* — Six different specimens of the salt were analyzed, in order to establish the presence or absence of accidental impurities.

In the first place, five hundred grams of the purest strontic nitrate of commerce were dissolved in two litres of pure water, and four times in succession a cubic centimeter of pure sulphuric acid, diluted with much water, was added to the solution. Each time only a small amount of precipitate appeared at once, the rest appearing slowly. After waiting in each case three or four days, the clear liquid was decanted. No barium could be found even in the first precipitate of strontic sulphate; but it is true that the spectroscope is not a very satisfactory means for the detection of barium under these circumstances. The acid solution of strontic nitrate, which had been thus almost if not quite freed from a possible trace of barium, was evaporated to small bulk, filtered from the precipitated strontic sulphate, and twice successively brought to crystallization. Each mass of crystals was washed three times with alcohol upon the filter pump, to free it from the mother liquor, which might contain calcium or magnesium. After having been converted into pure carbonate by precipitation with ammoniac carbonate and long continued washing the strontium was combined with bromine. For this purpose hydrobromic acid remaining from the barium work, obtained by repeated fractional distillation of the common acid, was used.

The strontic bromide was evaporated in a platinum dish. This was slightly attacked, bromine having been set free by a little occluded strontic nitrate in the carbonate. After evaporation to dryness the bromide was fused at a bright red heat in platinum. The alkaline solution of the fused cake was treated with hydric sulphide, filtered, acidified with hydrobromic acid, warmed, filtered from the platinic sulphide, boiled to free it from sulphuretted hydrogen, again filtered, and crystallized twice from water. The crystals were washed with alcohol, and the strontic bromide thus obtained is numbered I. below; it was used for the three preliminary experiments, as well as for Analysis 13.



The second sample of strontic bromide was prepared from similarly treated strontic nitrate which had been recrystallized four times instead of twice. The nitrate was converted into oxide by ignition in a nickel crucible; and the dissolved residue was filtered to get rid of a small amount of nickel. Ammonic sulphhydrate gave no trace of coloration to a portion of the filtrate. Two recrystallizations in a platinum bottle sufficed to free the strontic hydrate from a trace of undecomposed oxides of nitrogen, and the last crystals dissolved to form an absolutely clear solution in pure hydrobromic acid.\* The solution of strontic bromide was evaporated to crystallization, the crystals were dehydrated, and the anhydrous salt was fused; finally, after solution, standing, and filtration, a fresh crop of crystals was obtained. This sample, labelled No. II., was used for Analysis 14.

Among several different methods for obtaining pure strontic salts, that recommended by Barthe and Falières† seemed to promise well and accordingly the third preparation was based upon their work. The so called "pure" strontic chloride of commerce was dissolved in water, treated with ammonic hydrate and a little carbonate, and filtered from the precipitate containing iron, aluminum, and so forth. To the filtrate was added an excess of sulphuric acid, and the precipitated strontic sulphate was thoroughly washed with dilute sulphuric acid and then with pure water, in the hope of freeing it from magnesium and calcium. When the wash water became neutral to methyl orange the precipitate was treated with enough ammonic carbonate solution to convert about half of it into carbonate, and the mixed precipitate was then washed with water by decantation until only a very small constant trace of sulphuric acid (due to strontic sulphate) was found in the decantate. The carbonate was then decomposed by pure hydrochloric acid, and the solution was allowed to stand in a glass flask for nine months over the undecomposed sulphate, with occasional shaking. The strontic chloride was decanted, the sulphate was washed once with water, and the filtered decanted liquid was evaporated in a platinum dish until most of the free hydrochloric acid had been expelled. The dissolved residue was neutralized with ammonia, shaken with a little ammonic carbonate, and then filtered. To the greatly diluted filtrate was added an excess of pure ammonic carbonate, and the precipitate was washed until the wash water was free from chlorine. The strontic carbonate was dissolved in nitric acid which had been

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\* See these Proceedings, XXVIII. 17, bottom of page.

† Journ. Chem. Soc., Abs. 1892, p. 1277. Bull. Soc. Chim., [3.], VII. 104.

twice distilled in platinum, and the nitrate was crystallized twice successively in a platinum dish. Each quantity of crystals was washed with small quantities of water and three or four additions of alcohol. The first mother liquor, upon being fractionally precipitated by means of alcohol, showed distinct traces of calcium in the extreme solution; thus Barthe and Falières's method was not capable of freeing the substance wholly from calcium. The second mother liquor showed no trace of calcium upon the most careful scrutiny.

Two hundred grams of the purest crystals, after having been dried at  $130^{\circ}$ , were dissolved in about a litre of the purest water and filtered into a large platinum dish, into which was passed first pure ammonia gas and then pure carbon dioxide through a platinum tube.\* The pure strontic carbonate was washed by decantation eight or ten times, dried on the steam bath, and ignited in a double platinum crucible over a spirit lamp.

Part of this carbonate was converted into bromide by means of the purest hydrobromic acid,† and the product was digested for a long time with a considerable excess of carbonate. After filtration and evaporation the strontic bromide was fused in a platinum dish over the spirit lamp, the salt being perfectly clear while liquid. The translucent cake was dissolved, allowed to stand, filtered, faintly acidified with hydrobromic acid, and crystallized twice from water. Each time the crystals were washed with the purest alcohol. The resulting bromide of strontium was used for Analyses 1, 2, 3, 5, 6, 7, 12, 15, 16, 17, and 18.

The next sample was prepared from the strontic carbonate which had been digested with the strontic bromide just described. It was dissolved in the purest hydrobromic acid and purified much as before, except that the salt was fused twice with intermediate crystallizations, instead of only once. This fourth preparation was used for Analysis 9.

The fifth sample was made by the repeated crystallization of the combined mother liquors obtained from the four previous preparations. It was used for Analyses 4, 8, and 19.

The sixth preparation of strontic bromide was made from the strontic sulphate remaining from the third. This residue was treated with enough ammoniac carbonate to convert all but about twenty grams of

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\* See page 379.

† Prepared from pure baric bromide and redistilled many times. See these Proceedings, XXVIII. 17.

the sulphate into carbonate. The washed strontic carbonate having been dissolved in a slight excess of hydrochloric acid, the residual sulphate was allowed to remain in the solution for a week. After filtration, evaporation to dryness in platinum, solution, a second filtration, treatment with a little ammoniac hydrate and carbonate, and yet another filtration, the strontic chloride was converted into carbonate by means of purified ammoniac carbonate.\* After a very complete washing the strontic carbonate was dissolved in pure nitric acid in a platinum dish. The nitrate was crystallized, dried at 150°, recrystallized, washed with alcohol with the aid of the pump, dried, dissolved, and stirred with a little pure strontic carbonate for a week. The filtrate containing pure strontic nitrate was diluted, brought to boiling in a platinum dish, and poured in a fine stream into a boiling solution of pure ammoniac oxalate † also contained in platinum. The strontic oxalate was washed with the purest water upon the filter pump, until no ammonia could be detected upon boiling the filtrate with sodic hydroxide. Nessler's reagent still showed a trace of ammonia; but since this could easily be expelled by ignition, and the precipitate was very hard to handle, the washing was not carried further. After drying and powdering, the oxalate was converted into carbonate by ignition at a full red heat. The product was now ground in a mortar with an equivalent amount of pure ammoniac bromide, ‡ and the whole was gently ignited in a large platinum dish until no more ammonia was evolved. The hundred grams of strontium bromide thus obtained formed a pure white translucent cake upon fusion in a large platinum crucible. The cake was dissolved in water, and the alkaline solution, after having been boiled for some time, was neutralized with sulphuric acid. The clear filtrate from the strontic sulphate was now evaporated to a volume of about a hundred and twenty cubic centimeters, and diluted with two hundred cubic centimeters of the purest alcohol. The mixture was allowed to stand for a day, in order that the strontic sulphate and any trace of baric sulphate which might remain should be precipitated, and then filtered. After three successive crystallizations from water, the substance was used for Analysis 10; a further crop of crystals from the purest mother liquor served for Analysis 11.

Considering the pains taken in the purification of even the least pure sample, it is not surprising that all of these samples gave quantitative results which proved them to be essentially identical.

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\* See page 379.

† See page 379.

‡ See page 380.

*Silver.* — The preparation of pure silver has been repeatedly detailed. The most elaborate method described in the paper upon barium was used in the present case.\* A few improvements were introduced, notably the purification of the sodic hydrate used for the reduction of the argentic chloride by means of a strong galvanic current, instead of by hydrogen sulphide. Little but iron was found in it, however. The final crystals of electrolytic silver were usually fused upon pure sugar charcoal or lime, in a reducing flame; once however (for Analysis 10) the crystals contained in a lime boat within a stout porcelain tube were fused in a Sprengel vacuum by means of a Fletcher furnace. Two holes bored through the furnace at right angles to the flame entrance served to admit the tube. The heat was very gradually applied, and after the silver had been melted all the apertures of the furnace were closed and the tube was allowed to cool very slowly. A wide glass tube set into the porcelain tube on one end served as a convenient window for the observation of the fusion.

*Ammonic Carbonate.* — Two varieties of ammoniac carbonate were used for the work just described. The first consisted of ordinary pure "ammonic carbonate," which had been dissolved, treated with a small amount of a pure strontium salt, and filtered. This treatment undoubtedly removed any substance which could seriously interfere with the preliminary purifications for which this ammoniac carbonate was used. For the final stages of the purification of the strontium preparations, ammoniac carbonate was made by saturating the purest water in a platinum vessel with ammonia gas obtained by boiling the pure strong ammonia of commerce, and then passing into this saturated solution pure carbon dioxide. This latter gas was prepared by the action of dilute nitric acid on marble; it was purified by passing through washing flasks containing water and a meter of glass tube packed with moist beads. Upon delivering the gas into a Bunsen flame, no trace of calcium could be detected spectroscopically. Both gases were conducted into the solution through a platinum tube made for the purpose. The resulting ammoniac carbonate undoubtedly contained more or less of the amines common in ordinary ammonia, but it could not have contained a trace of non-volatile impurity capable of contaminating the strontic carbonate for whose preparation it was designed.

*Ammonic Oxalate.* — This salt was made by neutralizing pure ammonia water with pure oxalic acid, which had been still further

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\* These Proceedings, XXIX. 64, 65.

purified by many recrystallizations from hydrochloric acid and water. The ammoniac oxalate was crystallized twice in a platinum dish, the crystals being thoroughly washed each time. The salt was wholly free from chlorine.

*Ammoniac Bromide* was prepared in the usual fashion from ammonia prepared in platinum and bromine purified according to Stas. The reaction was naturally conducted in a flask of hard glass; but the crystallization was carried on as usual in platinum. A slight excess of the pure white substance precipitated 3.97970 grams of argentic bromide (fused, reduced to the vacuum standard) from a solution containing 2.28616 grams of pure silver. From this experiment  $\text{AgBr} : \text{Ag} = 100 : 57.4455$ . Stas found 57.445, hence the purity of the ammoniac bromide is proved.

A very simple and convenient platinum condenser was used for the preparation work described above. The tube, almost a centimeter in diameter and perhaps twenty-five centimeters in length, is bent, somewhat contracted near one end, and surrounded with a condenser jacket. It is easy to draw out the neck of a round-bottomed flask to fit outside of the conical end, and if the juncture is not absolutely tight a thin film of condensed liquid soon makes it so. If the glass neck be prolonged somewhat above the point of juncture, evaporation from this film is very slow. Of course pure filter paper may be used to tighten the joint if water is to be distilled. The apparatus has the great advantages of cheapness and transparency over the ordinary platinum still. All the hydrochloric, hydrobromic, sulphuric, and nitric acids, water, and alcohol used in the important stages of the work were distilled with the help of this contrivance.

Platinum vessels have been used wherever it was possible to use them in the work detailed above, although the fact is not always mentioned. They were cleaned in the usual fashion.

#### METHOD OF ANALYSIS.

As in the case of baric bromide,\* the silver required to precipitate all the bromine in strontic bromide was determined, as well as the amount of argentic bromide formed by the precipitation.

The chief problem which presented itself was the preparation of pure dry neutral bromide of strontium for weighing. In preliminary analyses the salt was ignited or fused in a platinum crucible, and

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\* These Proceedings, XXVIII. 23.

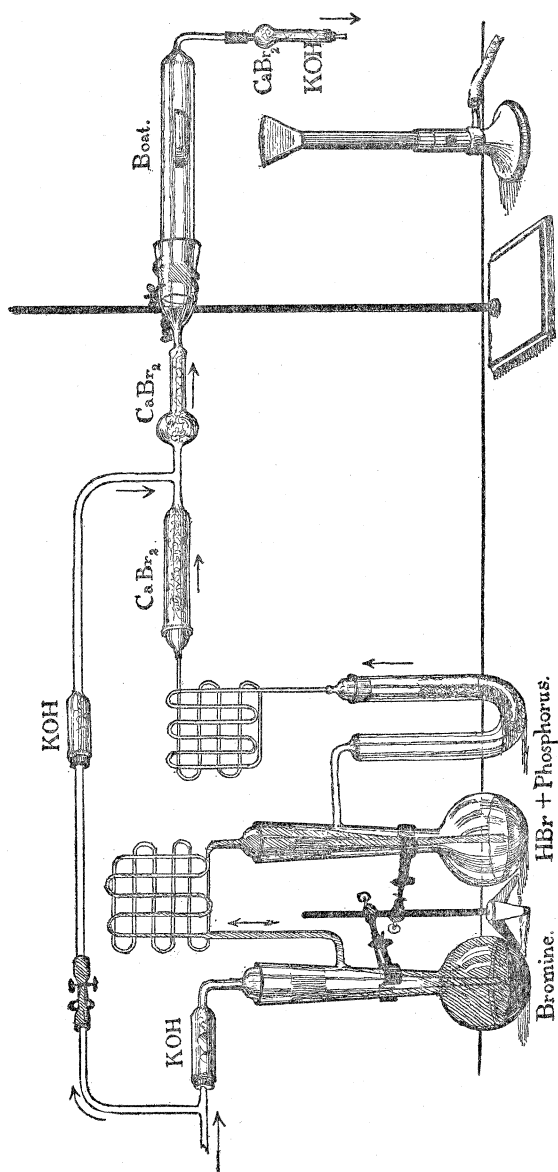
weighed as the baric bromide had been. The decomposition of the salt was so great, however, that the uncertainty of the alkalimetric correction sometimes amounted to two or three tenths of a milligram; hence this method was clearly inadmissible.

The fusion of the salt in a platinum boat in a stream of nitrogen gave much better results, and two or three further preliminary determinations by this method gave promise of much greater accuracy. It is probable that the slight decomposition which occurred even in the atmosphere of nitrogen was due to the presence at  $250^{\circ}$ – $300^{\circ}$  of a slight trace of moisture.

The presence of an excess of hydrobromic acid must necessarily lessen or prevent this decomposition; hence in three succeeding determinations (Nos. 13, 14, 15, below) pure dry hydrogen bromide was added to the nitrogen in which the combustion was conducted.

In these cases, however, the platinum boat, which had previously remained quite constant in weight, was evidently attacked, since upon one occasion (Exp. 15) it lost over two tenths of a milligram, and the pure white strontic bromide became tinged with a brown color. The weight of the boat *after* each fusion was taken as the true weight, because the bromide of platinum, if formed, must precipitate nearly as much silver as the bromide of strontium.

In order to avoid the corrosion of the boat, hydrogen was added in small quantities to the mixture of gases. This, by preventing the dissociation of the hydrobromic acid, effectually preserved the platinum, and the boat remained constant in weight. The pure translucent or transparent colorlessness of the fused salt left nothing to be desired. A somewhat complex piece of apparatus was needed for the purpose. (See page 382.) A mixture of six volumes of pure nitrogen (made by passing air and ammonia over red-hot copper) and one volume of pure hydrogen was delivered from a gas holder through a succession of tubes of red-hot copper, dilute chromic and sulphuric acids, concentrated alkaline pyrogallol, and fused potash, into the arrangement for preparing hydrobromic acid. This, as well as all the apparatus following, was without rubber connections, the ground joints being made tight by means of syrupy phosphoric acid (Morley) and flexible by means of fine glass gridirons (Finkener). The pure dry nitrogen and hydrogen were led in the first place into a flask containing bromine, and then over asbestos and red phosphorus saturated with pure fuming hydrobromic acid. The bromine and hydrobromic acid were proved to be pure by the usual quantitative analysis, and the red phosphorus was ground and washed many times with pure water to



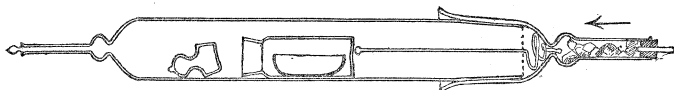
APPARATUS FOR FUSING STRONTIC BROMIDE.

Pure dry nitrogen and hydrogen enter the apparatus through the tube at the left. The arrangement for preparing this mixture is not shown. Upon closing the pinchcock in the upper left hand corner, the gases are driven through the flasks and charged with dry hydrobromic acid; upon opening the pinchcock, the hydrostatic pressure below causes the gases to flow through the upper short-cut tube and effectually sweep out the acid from the fusion tube. This latter tube, containing the boat in which the strontic bromide is fused, is at the right of the figure.

free it as much as possible from chlorine (Stas). The mixture of pure slightly moist hydrogen bromide, nitrogen, and hydrogen was now dried by calcic bromide free from chlorine and iodine, and thus became ready for use.

The hard glass tube used for heating the platinum boat containing the strontic bromide was ground very tightly into its socket of soft glass, since it was not advisable to risk the presence of phosphoric acid here. The powdered nearly anhydrous strontic bromide, having been packed tightly into the boat and carefully pushed into position in the fusion tube, was thoroughly dried at  $200^{\circ}$  in a stream of pure air. The elaborate apparatus for preparing the mixture of gases was now connected with the fusion tube, and when all the air had been expelled the boat was slowly heated to cherry-redness until the strontic bromide was wholly fused. The temperature was then allowed to fall a little below  $600^{\circ}$ , and the solidified bromide of strontium was freed from any possible excess of hydrobromic acid by a current of dry hydrogen and nitrogen free from acid, delivered through a short-cut tube (see page 382).

The almost red-hot boat was now transferred as quickly as possible to the light weighing bottle, within which it was allowed to cool. In the preliminary work (and in Analyses 13 and 14) this bottle was stoppered at once and cooled in an ordinary desiccator. Subsequently an improved desiccator was devised for this purpose. A wide glass tube capable of containing the weighing bottle was drawn out at one end to a fine tube, which was fitted with a ground-glass stopper. The other open end was made slightly conical and ground into a receptacle which was in its turn attached to a drying tube containing fused potash. The following sketch supplements this description.



While the boat was still hot within the fusion tube, the stopper of the weighing bottle was placed in the horizontal desiccator tube. The moment after the transference of the boat into the bottle, both together were slid into the momentarily opened desiccator tube by means of a glass rod which projected from the receptacle. The bottle was held by means of a glass carriage during this manipulation.

The open weighing bottle, with its stopper and fused contents, could now be heated indefinitely in a current of pure dry air at any tem-



perature below the softening point of soft glass. At the moment when it was desired to close the bottle, it was only necessary to elevate the desiccator tube from the horizontal to the vertical position, and the hot stopper fell automatically into the equally hot bottle. The desiccator tube was now closed above, and allowed to cool at least four hours in the balance room. It is needless to say that before taking the final weighing of the bottle its stopper was loosened.

Having thus obtained as nearly as possible the true weight of the typical salt of strontium, the remainder of the analysis was conducted in a manner essentially similar to that adopted in the case of baric bromide.\* Since it is unnecessary to describe again most of the precautions, nothing will be noted below excepting those particulars in which the details of the work differed from those already given. Two analyses, which were vitiated by known errors, are omitted from the tables.

#### THE RATIO OF SILVER TO STRONTIC BROMIDE.

*First Series.*—In this series a slight excess of silver was taken, dissolved, and diluted with at least a hundred times its weight of water, and added to the strontic bromide in a glass-stoppered flask. After the usual long continued shaking, the precipitate was collected upon a Gooch crucible, and the excess of silver in the evaporated filtrate and first five or six wash waters was determined after Volhard's method.† Upon subtracting this small excess of silver from the total, the amount corresponding to the strontic bromide remains. This method is not a very satisfactory one, the final result being probably too low, because of loss of a portion of the slight excess of silver.

*Second Series.*—Here the end point of the reaction was determined by titration after the method of Abrahall,‡ very weak solutions of silver and hydrobromic acid being used to titrate backwards and forwards. The mean reading was taken in each case, and the method of procedure resembled exactly the work with barium. These results are much more trustworthy than the last. In several cases the sample of strontic bromide was first analyzed by this method, and subsequently an excess of silver nitrate was added and the preceding method was applied.

*Third Series.*—For this series a new method was devised. Accord-

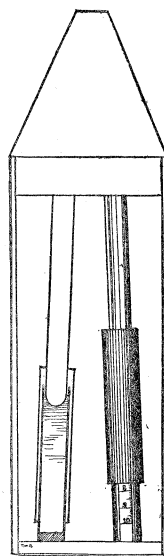
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\* These Proceedings, XXVIII. 24.

‡ These Proceedings, XXVIII. 24.

† These Proceedings, XXIX. 66.

ing to Stas,\* argentic bromide is wholly insoluble in water; according to Goodwin,† it is only very slightly soluble; while according to Kohlrausch and Rose,‡ it is soluble to the extent of three tenths of a milligram in a litre. The time during which chloride of silver is shaken makes an enormous difference in the solubility, and it is not impossible that a similar effect may occur here. Perhaps Kohlrausch and Rose did not agitate their precipitate so thoroughly as Stas did. According to the present experience the purest silver bromide was capable of yielding a filtrate which would give a very faint opalescence with both silver and hydrobromic acid; and this effect usually diminished upon long continued agitation. The method of determination used in this series was based upon this fact. Somewhat less silver than the amount required was added to the strontic bromide, and a very weak standard solution of argentic nitrate (the cubic centimeter contained a milligram of silver) was dropped in until equivalent solutions of silver and hydrobromic acid produced equal opalescence in two similar pipetted portions of the supernatant liquid. Since the opalescence was so faint that one could only with difficulty see it at all under ordinary conditions, a piece of apparatus, which may be named a "nephelometer" (*νεφέλη*, a cloud), was devised for detecting it. Two test tubes, holding each just thirty cubic centimeters, were arranged in a wooden frame so that two centimeters of the top of the tubes were in darkness. The bottoms of the tubes were fitted into the top of larger opaque tubes containing water, and were provided with closely fitting cylindrical shades, which could be raised or lowered independently over a graduated scale. All these contrivances prevented disturbing side reflections from the meniscus at the top of the tube and the rounded glass at the bottom. The two test tubes were slightly inclined towards one another, so that the eye at a distance of eight inches could look directly into both without change of position. Filled with pure water the tubes appear absolutely black, even when exposed to a strong light; but an absurdly small amount of precipitate, which no ordinary means



NEPHELOMETER.

\* Mém. de l'Acad. Belg., XLIII., Part II. Introduction.

† Zeitschr. f. phys. Chem., XIII. 645.

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‡ Ibid., XII. 234.

could discover at all, makes a very evident cloudiness. By sliding the shades up and down a point may be found where the two tubes, containing solutions of different cloudiness, appear equal in depth of tone. The reason of this is that only the portion of the opalescence is visible upon which light is allowed to fall. Of course the intensities of the opalescence, and hence the quantities of precipitate, are then inversely as the length of the lighted portions of the two tubes.

If care is taken to direct the light horizontally upon the tubes, considerable accuracy may be obtained with the apparatus, especially if the columns are nearly equal in cloudiness.

A pointed blackened roof with a small hole in the top for the eye is useful in excluding light from the surface of the liquid, thus rendering the comparison easier. The chief advantages of the apparatus lie in the facts that the two disks of light to be compared remain equal in size throughout the comparison, and that the eye is not confused by bright surface reflections. Two typical test series are given below. In each case one shade was adjusted at ten centimeters, and the other was run backward and forward until apparent similarity was obtained.

(a.) One tube contained 0.010 milligram of silver, and the other 0.0125 milligram, measured by means of a very dilute standard solution. Both amounts were made up to twenty-five cubic centimeters, and one cubic centimeter of hundredth normal hydrochloric acid was added to each. The opalescence in each was then compared after a thorough stirring and a short delay.

#### HEIGHTS OF COLUMNS APPEARING ALIKE.

	Stronger Solution.	Weaker Solution.
	8.7 cm.	10.0 cm.
	7.9 "	10.0 "
	6.9 "	10.0 "
	7.6 "	10.0 "
	8.4 "	10.0 "
	8.6 "	10.0 "
	8.9 "	10.0 "
Found,	8.1 cm.	10.0 cm.
True value,	8.0 "	10.0 "

(b.) In a similar experiment one tube contained 0.025 milligram of silver, the other 0.0225 milligram.

## HEIGHTS OF COLUMNS APPEARING ALIKE

	Stronger Solution	Weaker Solution
	8.8 cm.	10.0 cm.
	8.9 "	10.0 "
	8.2 "	10.0 "
	9.5 "	10.0 "
	8.9 "	10.0 "
	8.7 "	10.0 "
	8.9 "	10.0 "
	9.4 "	10.0 "
Found,	8.9 cm.	10.0 cm.
True value,	9.0 "	10.0 "

Some series were more accurate, others less so, than these, which serve to give a fair idea of the probable error of the method.

The details of the analysis must be evident from what has been said. The method is similar to Stas's third method for the determination of chlorine,\* except that of course the opalescence is very much fainter.

Below are given the tables containing the data and results of the three series; these will be comprehensible without further remark.

## RATIO OF STRONTIC BROMIDE TO SILVER

## First Series. Volhard's Method.

No. of Analysis.	No. of Specimen	Weight of Strontic Bromide taken.	Total Weight of Silver taken.	Excess of Silver	Weight of Silver corresponding to Strontic Bromide.	Ratio $\frac{\text{SrBr}_2}{\text{Ag}_2}$	Atomic Weight Sr
1	III.	grams 1.49962	1.30893	m. g 1.38	1.30755	114.689	87.658
2	III.	2.41225	2.10494	1.43	2.10351	114.677	87.633
3	III.	2.56153	2.23529	1.72	2.23357	114.683	87.645
4	V.	6.15663	5.3086	0.2	5.3684	114.683	87.644
		12.63003			11.01303	114.683	87.644

\* See these Proceedings, XXIX 86.

## RATIO OF STRONTIC BROMIDE TO SILVER.

## Second Series Abrahall's Method

No of Analysis	No of Specimen.	Weight of Strontic Bromide taken.	Weight of Silver required	Ratio $\frac{\text{SrBr}_2}{\text{Ag}_2}$	Atomic Weight of Strontium.
5	III.	grams. 1.49962	grams. 1.30762	114.683	87.645
6	III.	2.41225	2.10322	114.693	87.667
7	III.	5.24727	4.57502	114.694	87.668
8	V	6.15663	5.3680	114.691	87.663
		15.31577	13.35386	114.692	87.663
Third Series. New Method.					
9	IV	grams. 2.9172	grams. 2.5434	114.697	87.675
10	VI	3.8946	3.3957	114.692	87.665
11	VI.	4.5426	3.9607	114.692	87.664
12	III	5.2473	4.5750	114.695	87.671
		16.6017	14.4748	114.694	87.668

## RATIO OF ARGENTIC TO STRONTIC BROMIDE.

In many of the preceding determinations the bromide of silver resulting from the decomposition was weighed. In every case a slight excess of silver nitrate was added, to render the argentic bromide wholly insoluble in the filtrate. The very slight amount which may have been dissolved by the wash water during its brief contact with the precipitate was not considered. The precipitate was collected upon a Gooch crucible; and the traces (0.04 to 0.2 milligram) of asbestos carried through were collected upon a small washed filter, ignited separately, weighed, and added to the gain in weight of the crucible. From this was subtracted the loss in weight of the precipitate upon fusion in a covered porcelain crucible. A description of the dark room used for the experiments, and many other precautions and details, will be found in other papers.\* The results are tabulated below.

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\* These Proceedings, XXVIII. 24; XXIX. 74.

RATIO OF STRONTIC AND ARGENTIC BROMIDES.

First Series.

No of Analysis	No of Specimen.	Weight of Strontic Bromide taken	Weight of fused Argentic Bromide found	Ratio $\frac{\text{SrBr}_2}{2 \text{ AgBr}}$	Atomic Weight of Strontium.
13	I.	grams 1 6086	grams 2 4415	65 886	87 669
14	II.	1 8817	2 8561	65 884	87 662
15	III	4 5681	6 9337	65 883	87 657
		8 0584	12 2313	65 8834	87 660
Second Series					
16	III.	grams 1 49962	grams 2 27625	65.881	87 652
17	III	2 41225	3 66140	65 883	87 660
18	III	2 56153	3 88776	65 887	87 674
19	V	6 15663	9 34497	65 882	87 654
		12 63003	19 17038	65 883	87 659

It remains only to bring together the results into one table.

FINAL AVERAGES

Oxygen = 16.000

			Strontium equals
I.	2 Ag : SrBr <sub>2</sub>	First Series	87.644
II.	“ “	Second Series	87.663
III.	“ “	Third Series	87.668
IV.	2 AgBr : SrBr <sub>2</sub>	First Series	87.660
V.	“ “	Second Series	87.659
		Total average	= 87.659
		Average, rejecting I. above	= 87.663

The last average is probably most nearly correct.

The analysis of strontic chloride has already been begun, and the preliminary results indicate that the results given above are certainly not too high. For the present, then, the atomic weight of strontium may be taken as 87.66 if oxygen is 16.00, 87.44 if oxygen is 15.96, and 87.01 if oxygen is 15.88.